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Hydrodeoxygenation of Guaiacol over Al-MCM-41 Supported Metal Catalysts: A Comparative Study of Co and Ni

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Abstract

The hydrodeoxygenation (HDO) of guaiacol, a model compound of pyrolysis oil, was catalyzed by Al-MCM-41 supported Co and Ni catalysts in a fixed-bed continuous reactor at ambient pressure. The effects of contact time (W/F) and reaction temperature on HDO of guaiacol over the Co and Ni catalyst were studied. Cobalt showed higher activity than nickel in HDO via C–O hydrogenolysis pathway. The conversion of guaiacol over Ni catalyst principally occurred via C–C hydrogenolysis pathway, resulting in methane formation. Besides, the acidic Al-MCM-41 support catalyzed the methyl transfer reaction to form the methylated products. Additionally, increasing reaction temperature improved the HDO and suppressed the hydrogenation but promoted the methanization activities.

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Keywords: Hydrodeoxygenation; Hydrogenolysis; Nickel; Cobalt; Al-MCM-41; Guaiacol.

1. Introduction

Pyrolysis of lignocellulose biomass has attracted much interest lately because it presents a potential for producing the alternative liquid fuel from the abundance of bioresource [1–3]. Although the pyrolysis oil has the storable and

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transportable advantages, direct utilization of this product is very difficult due to its high oxygen content, resulting in low heating value and low thermal stability [2, 4]. Hence, upgrading process via deoxygenation is required to obtain the value petrochemical and fuel from pyrolysis oil [1, 5]. Catalytic hydrodeoxygenation (HDO) is a promising process for pyrolysis oil upgrading since it can enhance the C/O ratio [6, 7]. As the pyrolysis oil contains a large amount of phenolic derivatives (e.g. phenol, cresol, guaiacol, methyl-guaiacol) [3, 8], these phenolic compounds were used as model compounds in the HDO studies [6, 9, 10].

To date, there have been numerous studies of different types of HDO catalyst, such as noble metals (e.g. Ru, Pd and Pt) [1, 11, 12], base metals (Cu, Fe, Co and Ni) [13–15], transition metal sulfides (CoMoS and NiMoS) [16, 17] and transition metal phosphides (Ni_2P and Co_2P) [2, 18–20]. Noble metal was found as an unsuitable HDO catalyst due to its high activity in hydrogenation or gasification [1, 6]. On the other hand, Ni catalyst presented a higher gasification activity while Fe showed a lower HDO activity than noble metals [6, 9, 13]. Adding Fe to Pd or Ni catalysts changed the selectivity from ring saturation to direct deoxygenation, resulting in oxygen-free aromatic products [6, 21, 22]. Moreover, conversion of guaiacol over transition metal phosphide catalysts mainly produced phenol and catechol; and very high contact time (W/F) was required to produce the oxygen-free aromatic products [18–20].

Besides metal function, the morphology and acidity of support also played an important role in HDO activity of catalysts. In HDO of guaiacol over iron-based catalysts, activated carbon showed much lower deoxygenation activity than silica due to its low phenolic adsorption ability [13]. Zhu et al. [23] figured out that the acidic HBeta zeolite catalyzed the transalkylation reactions but showed lower stability than SiO_2 support. During HDO of phenolic, coke deposit was observed on the surrounding area of metal as well as on the support, resulting in catalyst deactivation [5, 13, 24]. In addition, mesoporous supports exhibited a much higher stability than microporous supports [24, 25].

The purpose of this study is to compare the catalytic behavior of Co and Ni in HDO of guaiacol under different reaction conditions. Al-MCM-41 was chosen as the support because its acidity and mesoporosity might facilitate the HDO activity of catalysts. The HDO activity of these catalysts was investigated at different temperatures and contact time (W/F) in order to clarify the role of metal and support.

2. Experimental

2.1. Catalyst preparation

A mesoporous Al-MCM-41 support (ACS Material) was treated at 500 ^{o}C for 14 h in air. The catalysts were prepared by the wetness impregnation of aqueous solutions containing the specific amount of $Co(NO_3)_2.6H_20$ or $Ni(NO_3)_2.6H_20$ (Aldrich) to achieve the desired metal loading of 10 wt%. The impregnated catalysts were dried at 105 ^{o}C for 8 h and calcined at 500 ^{o}C for 14 h. The calcined catalysts were sieved to give the particles 35–60 mesh in the size range.

2.2. Catalyst characterization

The nitrogen adsorption and desorption isotherms were obtained using a TriStar II 3020 equipment at 77K. The TM3030 scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX) was used to measure the surface morphology and the distribution of Co and Ni on the supports.

Catalytic reaction of guaiacol was conducted in a fixed-bed reactor (I.D. 13 mm) made of stainless steel at atmospheric hydrogen pressure [5]. The Ni catalyst was reduced at 500 ºC while the Co catalyst was reduced at 450 ºC for 1 h in hydrogen flow according to the TPR result [5]. The catalytic reactions were conducted under the following conditions: catalyst mass of 0.5–2.0 g, pressure of 1.0–1.1 atm, temperature of 300–400 ºC, guaiacol liquid flow rate of 1.08 mL/h, and H_2 flow rate of 90 mL/min. The W/F is specified as the ratio of catalyst amount (g) to flow rate of guaiacol (g/h). The outlet was heated to minimize the heavy product condensation. The products were trapped with acetone in ice condenser. The condensed and non-condensed products were analyzed by GC-FID (Shimadzu GC-2014) and GC-TCD (Shimadzu GC-8A), respectively. The data used for each W/F and temperature

were collected at a time on stream (TOS) of 30 min. The guaiacol conversion and product yields were calculated in terms of carbon molar basis.

$$X_{Gua}\,(\%) = \frac{Mol(gua)_{in} - Mol(gua)_{out}}{Mol(gua)_{in}} \times 100 \quad (1)$$

$$Y_i\,(\%) = \frac{Mol_i \times \alpha_i}{Mol(gua)_{in} \times 7} \times 100 \quad (2)$$

where α_i is the number of carbon atoms in the molecule of product i.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the N_2 isotherms of Al-MCM-41 and metal supported catalysts. They exhibited typical type IV isotherms with inflection observed at 0.3–0.4 P/P_0. The presence of mesopores in support was confirmed by a H1-type hysteresis loop appeared in the isotherms. The metal modified catalysts had similar type isotherms to Al-MCM-41 support. However, it showed reduced textural properties due to the blockage of the pores by metal impregnation. Both support and metal modified catalysts had a narrow pore size distribution of 1.8–3.5 nm. The pore size distributions of Co and Ni catalysts were shifted to a smaller range compared to that of pure support. The EDX elemental analysis from SEM observation (Fig. 2) indicated that the Si/Al molar ratio of Al-MCM-41 support was around 14. The percentages of Co and Ni in the supported metal catalysts were 9.6 wt% and 9.7 wt%, respectively.

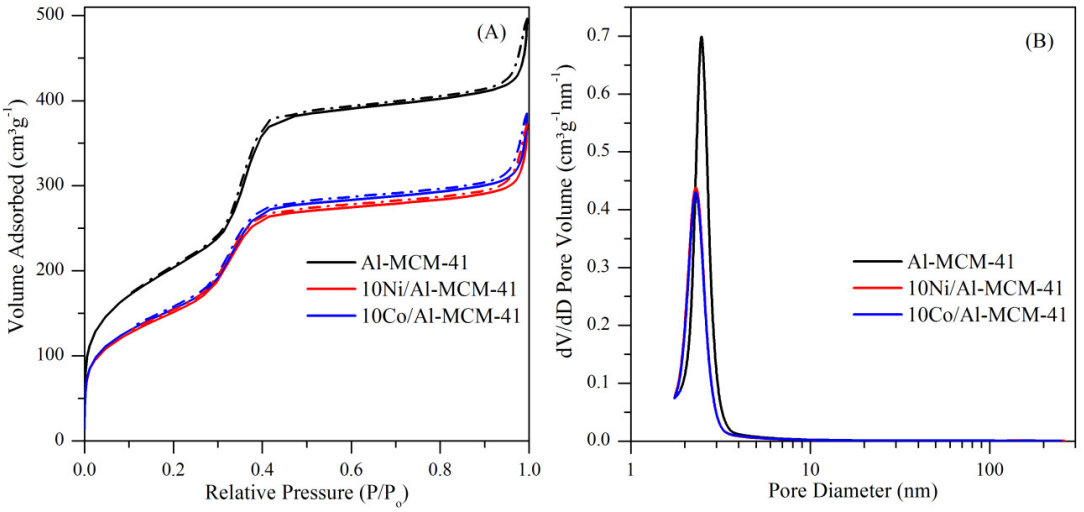

Fig. 1. N_2 adsorption (solid line)/desorption (dash–dot line) isotherms (A) and pore size distributions (B) of Co and Ni supported Al-MCM-41 catalysts.

3.2. Catalyst activity

The metal modified Al-MCM-41 catalysts were evaluated for HDO of guaiacol at temperatures from 300 to 400 ºC under ambient pressure. All the data points were obtained with the carbon balance between 91 and 99 %. The conversion of guaiacol on the bare support at 400 ºC mainly formed catechol, methane, and methyl guaiacol via demethylation and methyl transfer reactions catalyzed by the acidic sites. The details of the performance of this support are reported elsewhere [5].

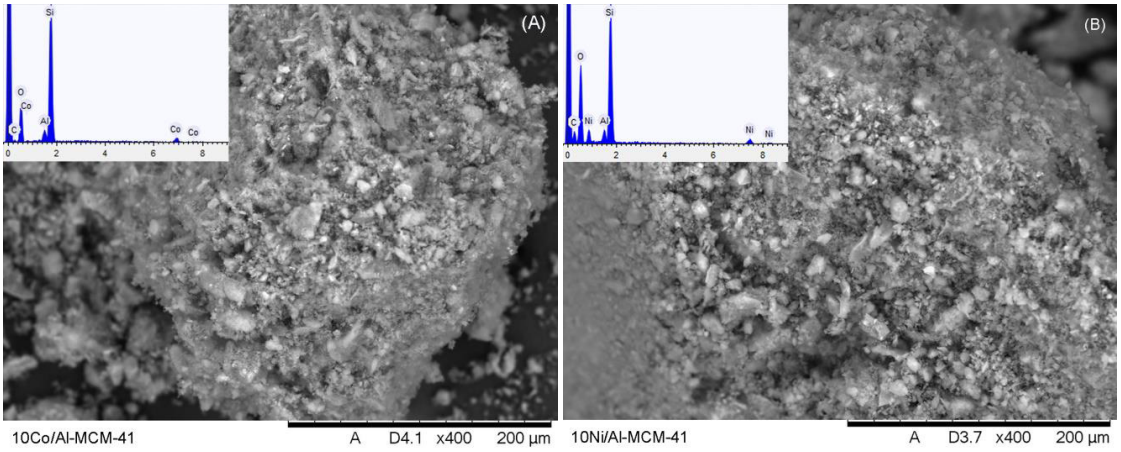

Fig. 2. SEM images plug EDX pattern of Co and Ni supported Al-MCM-41 catalysts

Fig. 3 illustrates the HDO activity of Co and Ni supported Al-MCM-41 catalysts as a function of W/F. The guaiacol conversion showed an insignificant difference between Co and Ni catalysts. However, product distribution revealed that the Co catalyzed the HDO of guaiacol to form oxygen-free aromatics (i.e., benzene, toluene, xylene, etc.) and monooxygenated aromatics (i.e., phenol, cresol, xylenol, etc.) while the Ni catalyzed the multiple C–C cleavages to form C1 products (mainly CH_4 and less than 0.7 % yield of CO_2 and CO). The Ni catalyst was recognized as a poor catalyst for vapor-phase HDO of guaiacol since it produced more dioxygenated aromatics at lower W/F or more methane at higher W/F compared with the Co catalyst.

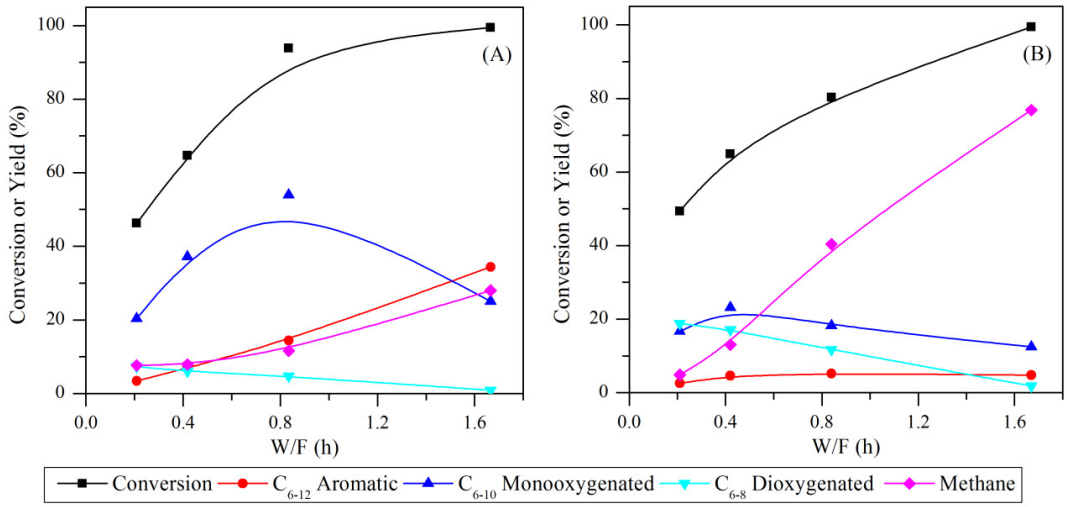

Fig. 3. Conversion and product yields of HDO of guaiacol. (A) Co/Al-MCM-41; (B) Ni/Al-MCM-41. Reaction condition: T = 400 °C, P = 1 atm, H_2/guaiacol molar ratio = 25, TOS = 30 min.

When increasing W/F, HDO activity of Co catalyst increased, resulting in the increase in oxygen-free aromatics yield and the decrease in dioxygenated aromatics yield (Fig. 3A). The C_{6-10} monooxygenated products, mainly hydroxyl derivatives, were observed as the intermediate of oxygen-free aromatics in HDO of guaiacol. At W/F of 1.67 h, the molar ratio of methane to reacted guaiacol became higher than the stoichiometric ratio (i.e. 1) if the methane was formed from only demethylation of guaiacol, suggesting that ring-opening took place. In HDO of guaiacol, the demethylation and ring-opening reaction are unavoidable at high temperatures [6, 23], yielding

methane in the gas phase. Interestingly, the existence of C_{7-12} aromatic and C_{7-10} phenolic implied that the methyl groups were also transferred to the aromatic rings instead of methane formation [20, 23]. These methyl transfer reactions catalyzed by the acid sites of Al-MCM-41 support helped to preserve the carbon in the liquid products.

The Ni catalyst changed the selectivity from dioxygenated products to methane when increasing contact time W/F (Fig. 3B). Oxygen-free aromatics yield was almost unchanged at the low level while the methane yield kept increasing with guaiacol conversion. In contrast to the Co catalyst, the Ni catalyst showed lower HDO and higher gasification activities, resulting in methane as a dominant product. Consistent with our study, Ni was also observed as an active site for multiple C–C hydrogenolysis, yielding methane in previous studies by Chen et al. [9] and Sitthisa et al. [26].

Fig. 4 demonstrates the effect of temperature on HDO activity over the Co and Ni catalysts. In general, the higher temperature resulted in the higher guaiacol conversion. Increasing the reaction temperature improved the deoxygenation and methanization activities of the Co catalyst and strongly enhanced the methanization activity of the Ni catalyst. Methane was observed as the major product of guaiacol HDO over Ni catalyst in all temperatures, gave the further confirmation of high C–C hydrogenolysis activity of Ni. There were no intermediate light hydrocarbon products (i.e. C_{2+}) in the gas phase at 400 ºC. However, a trace amount of ethane and methanol was observed at 300 ºC. These results suggest that the C–C hydrogenolysis occurred strongly and quickly at 400 ºC, resulting in C1 as final products. In addition, a trace amount (less than 0.7 %) of saturated ring products (i.e. cyclohexane and cyclohexanol) was observed at 300 and 350 ºC, and there was no observation of these products at 400 ºC. This suggests that lower reaction temperatures are favorable for the hydrogenation of aromatic rings [1, 4].

Guaiacol has been studied as a model compound due to its functional groups (i.e. methoxy and hydroxyl) representing for the pyrolysis oil components [3, 8]. In general, anisole yield was less than phenol yield in all experiments because the aromatic-methoxy group has a lower bonding dissociation energy compared to the aromatic-hydroxyl group [27]. Anisole was found as a minor product at 400 °C, and its yield increased when the reaction temperature decreased. This result implies that the HDO of both methoxy and hydroxyl groups is slowed down at lower reaction temperatures.

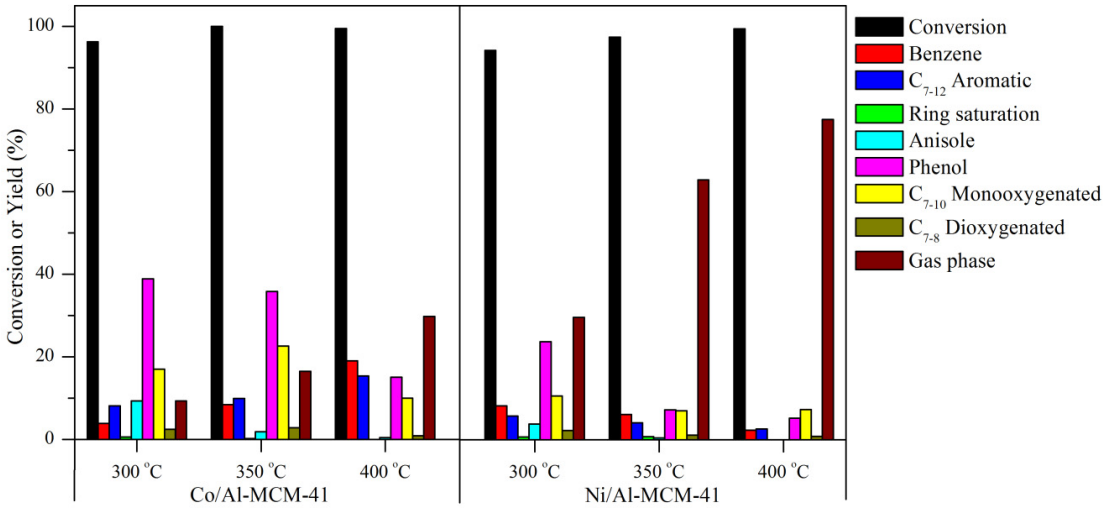

Fig. 4. Conversion and product yields of HDO of guaiacol on Co/Al-MCM-41 and Ni/Al-MCM-41. Reaction condition: P = 1 atm, H_2/guaiacol molar ratio = 25, W/F = 1.67 h, TOS = 30 min.

4. Conclusion

In gas phase HDO of guaiacol at ambient pressure, the Co catalyst presented a higher activity in deoxygenation compared with the Ni catalyst. Co catalyzed the hydrogenolysis of C–O bond to produce the oxygen-free aromatics while Ni catalyzed the hydrogenolysis of C–C bond to produce methane in the gas phase. The methyl transfers

occurred over acid sites of Al-MCM-41 support, yielding C_{7-12} aromatic and C_{7-10} phenolic products. The HDO and methanization reactions were enhanced significantly when the reaction temperature increased while the ring hydrogenation reaction was prohibited. Increasing reaction temperature promoted to deoxygenation more than methanization on the Co catalyst but only favored the multiple C–C hydrogenolysis on the Ni catalyst.

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